JOURNAL OF PURE APPLIED AND INDUSTRIAL PHYSICS
An International Open Free Access, Peer Reviewed Research Journal
www.physics-journal.org

ISSN 0976-5727 (Print)
ISSN 2319-8133 (Online)
Abbr:J. Pure Appl. & Ind. Phys.
2014, Vol.4(3): Pg.127-132

Effect of Anionic Size (Cl^- and I^-) on Ultrasonic Studies of Aqueous Solutions of NaCl and NaI at Different Temperatures

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(Received on: June 17, 2014)

ABSTRACT

The density, viscosity and ultrasonic velocity have been measured for aqueous solutions of NaCl and NaI at different temperatures. From these values, the parameters like free volume, free length, adiabatic compressibility and acoustic impedance were worked out. The experimental results were established the correlations with intermolecular interactions between solvent and solute. Conclusion was drawn how size of anions play important role in understanding the molecular interactions.

Keywords: Ultrasonic velocities, compressibility, acoustic impedance, free length, free volume, solute, solvent.

INTRODUCTION

Ultrasonic investigation provides an extensive application in characterizing thermodynamic and physiochemical behavior of liquid mixtures[1-3]. The studies of intermolecular interaction play an important role in the development of molecular sciences. In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids owing to its ability of characterizing physiochemical behavior of the binary and ternary mixtures[2-5]. The nature and extent of the patterns of molecular association and dissociation that exist in solutions have been investigated by ultrasonic techniques. The

nature of relative strength of molecular interactions between components of liquid solutions have been successfully investigated by ultrasonic methods Further, the measurement of excess thermodynamic properties are found to be very significant in studying the structural arrangements associated with the liquid solutions[6-8] Ultrasonic velocity studies have contributed significantly to chemical physics, industrial technology, biomedical sciences and food industries[9,10].

Therefore, the present work mainly deals with velocity studies pertaining to aqueous solutions of sodium chloride and sodium iodide. These salts are of significant importance in physiological processes of life. Many physiological processes depend on the concentrations of electrolytes and their interactions with aqueous medium in protoplasm of the cell[11] Nerve impulse also depends upon the concentration of aqueous solution of electrolytes. Hence, these electrolytes are chosen for the present investigation.

MATERIALS AND METHOD

All the chemicals used in this present work are analytical reagent (AR) grades; doubly distilled water has been used for preparing the solution of 0.125M to 2M aqueous electrolytic solutions. Higher concentration solutions prepared by weight and remaining solutions were prepared by dilution method. For weighing, an electronic digital balance having an accuracy of ±0.1 mg was used. Densities were determined using specific gravity bottle by relative measurement method with accuracy of ±0.1 $kg.m^{-3.}$ An Ostwald's viscometer was used for viscosity measurement. An ultrasonic interferometer having the frequency 2MHz (VI Microsystems Pvt Ltd, Perungudi, Chennai) with an accuracy of ±0.1% was used for velocity measurement. Constant digital temperature water bath was used to maintain the constant temperature with an accuracy of ±0.1K.

RESULTS AND DISCUSSIONS

The parameters are calculated on the basis of theory as given below:

Adiabetic compressibility can be calculated from speed of sound (U) and density (ρ) of the measurement.

$$\beta=1/U2\rho$$

Intermolecular free length can be determined as:

$$L_f = K\ \beta^{1/2}$$

Where K values from different temperatures were taken from the work of Jacobson[12].

The acoustic impedance is the product of the velocity of ultrasound in a medium and its density can be calculated by the relation[13],

$$Z = U\ \rho$$

The free volume (Vf) in terms of ultrasonic velocity (U) and the viscosity of liquid(n) as:

$$Vf = [Meff\ U / Kn]$$

Meff-effective molar mass, $K= 4.28x10^9$, n-viscosity of solution[14].

The ultrasonic studies of liquid mixture are important to investigate the molecular interaction in the solution. The

values of ultrasonic velocity, compressibility, free length, free volume and acoustic impedance may be affected by three factors. The first factor is the specific forces between molecules, such as hydrogen bond, charge-transfer complexes. If the values of the above parameters are greater than its ideal values, breaking of hydrogen bond (weaker hydrogen bonding) result and if the values are lesser than its ideal, strong hydrogen bonding result.

The second factor is the physical intermolecular forces, including electrostatic forces between charge particles and between permanent dipoles, induction forces between a permanent dipole and an induced dipole and forces of attraction (dispersion forces) and repulsion between non polar molecules. The physical intermolecular forces are usually weaker when the values of adiabatic compressibility and free length are greater and vice versa.

The third factor is the structural characteristics of the component, arising from geometric fitting of one component into other's structure, due to the differences in shape, size and free volume of the component.

In our present system, water molecules having hydrogen bonding which get affected due to the addition of electrolytes. All types of molecular interactions (hydrogen bonding, ion-dipole, dipole-dipole and dispersion forces) present in this system.

The values of ultrasonic velocity, density and viscosity of 0 to 2M concentrations of NaCl and NaI at 298.15K and 303.15K temperatures are presented in Tables 1 to 2. The acoustic parameters such as adiabetic compressibility, free length, free volume and acoustic impedance are presented in Tables-3 to 6.

Table -1: Molarity, ultrasonic velocity, density and viscosity for NaCl at 303.15K and at 298.15K

	303.15K			298.15K		
m	U(m/s)	ρ(Kg/m^3)	η(Nm^{-2}s)	U(m/s)	ρ(Kg/m^3)	η (Nm^{-2}s)
0.0	1504.35	995.54	797.5	1495.6	994.24	890.4
0.125	1513.19	997.09	780.8	1503.76	1000.92	896.38
0.25	1517.96	1004.27	798.5	1509.05	1003	911.08
0.5	1534.25	1012.97	817.5	1525.76	1013.6	927.19
1	1573.03	1044.11	861.4	1566.37	1042.08	966.57
2	1619.23	1070.31	908.6	1609.78	1068.29	1095.05

Table -2: Molarity, ultrasonic velocity, density and viscosity for NaI at 303.15K and at 298.15K

	303.15K			298.15K		
m	U(m/s)	ρ(Kg/m^3)	η (Nm$^-$s)	U(m/s)	ρ(Kg/m^3)	η (Nm^{-2}s)
0.0	1504.35	995.54	797.5	1495.59	994.24	890.4
0.125	1504.93	1002.35	808.95	1496.18	1005.64	887.74
0.25	1504.35	1013.35	811.77	1495.59	1011.71	880.16
0.5	1502.59	1033.51	821.74	1494.44	1033.5	892.5
1	1500.85	1128.89	857.08	1492.71	1115.12	955.86
2	1500.26	1167.01	872.07	1491.42	1164.75	983.5

Table -3: Molarity, compressibility, free length, free volume and acoustic impedance for NaCl at 303.15K

m	βx10-10(m^2N^{-1})	Lfx10^{-11}(m)	Vfx10^{-8}(m^3)	Zx10^6($Kgs^{-1}m^{-2}$)
0.0	4.4386	4.1798	6.4223	1.497
0.125	4.38	4.1522	7.0898	1.508
0.25	4.3215	4.1243	8.7739	1.524
0.5	4.1938	4.063	12.388	1.554
1	3.8706	3.9033	23.327	1.642
2	3.5634	3.7452	53.35	1.733

Table- 4: Molarity, compressibility, free length, free volume and acoustic impedance for NaCl at 298.15K

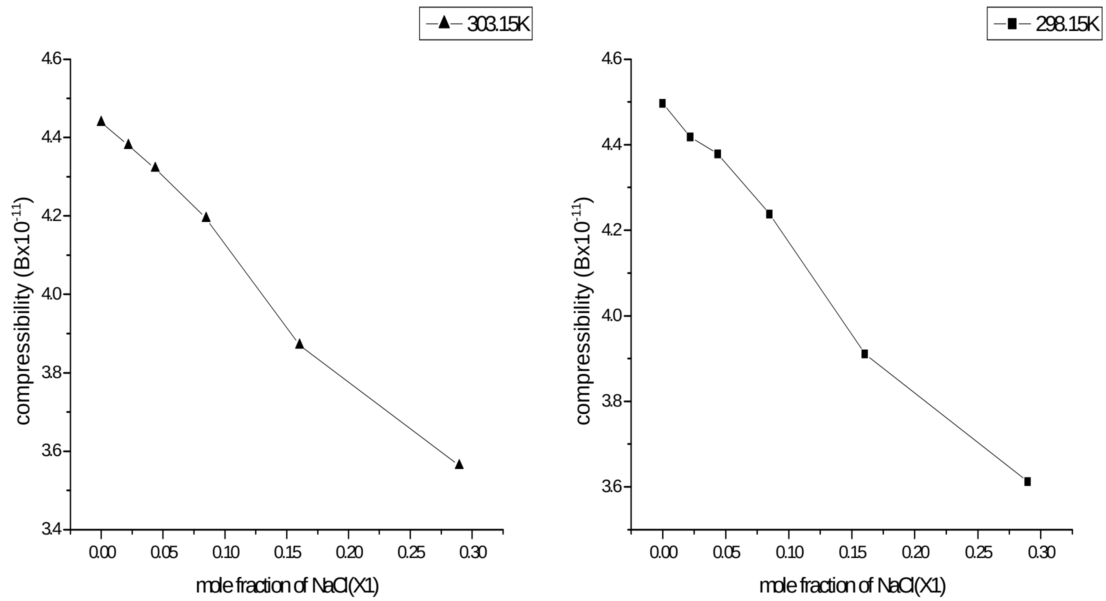
m	βx10-10(m^2N^{-1})	Lfx10^{-11}(m)	Vfx10^{-8}(m^3)	Zx10^6($Kgs^{-1}m^{-2}$)
0	4.4965	4.171	8.7833	1.486
0.125	4.4182	4.134	10.528	1.505
0.25	4.3782	4.115	12.8049	1.513
0.5	4.238	4.049	17.7757	1.546
1	3.1912	3.3027	32.5397	1.632
2	3.6122	3.738	75.2703	1.719

Table -5: Molarity, compressibility, free length, free volume and acoustic impedance for NaI at 303.15K

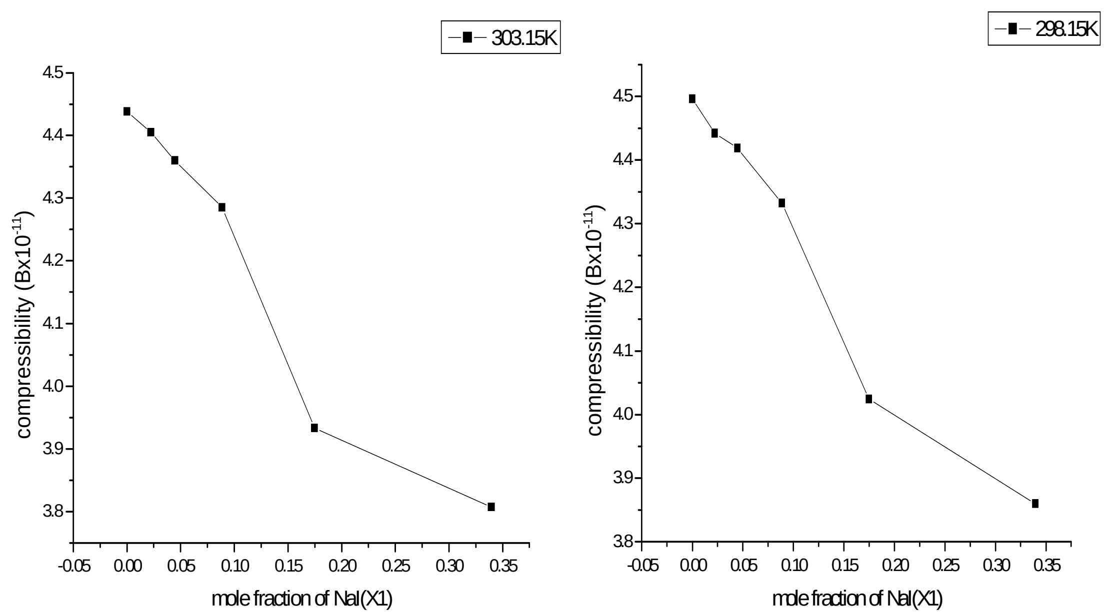
m	βx10-10(m^2N^{-1})	Lfx10^{-11}(m)	Vfx10^{-8}(m^3)	Zx10^6($Kgs^{-1}m^{-2}$)
0	4.4386	4.1798	6.4223	1.497
0.125	4.405	4.164	10.586	1.508
0.25	4.36	4.1429	15.817	1.524
0.5	4.285	4.1072	31.4	1.553
1	3.933	3.9344	93.836	1.694
2	3.807	3.8711	353.2	1.751

Table -6: Molarity, compressibility, free length, free volume and acoustic impedance for NaI at 298.15K.

m	βx10-10(m^2N^{-1})	Lfx10^{-11}(m)	Vfx10^{-8}(m^3)	Zx10^6($Kgs^{-1}m^{-2}$)
0.0	4.4965	4.171	8.783	1.487
0.125	4.4421	4.1457	13.748	1.504
0.25	4.4189	4.1349	19.811	1.513
0.5	4.3324	4.0942	39.579	1.544
1	4.0246	3.9461	128.056	1.664
2	3.8598	3.8644	497.75	1.737



Compressibility verses mole fraction of NaCl solution



Compressibility verses mole fraction of sodium iodide solution

From the above tables 1 to 2, it is observed that ultrasonic velocity, density and viscosity increased as concentration increased in case of NaCl. But in case of NaI, these values are decreased with respect to concentration. With respect to temperature, ultrasonic velocity is greater at high temperature and vice versa in both cases. Viscosity is lower at high temperature and vice versa.

On the basis of above graphs, it is found that adiabatic compressibility goes on decreasing as concentration increase and this indicates that strong solute-solvent interaction operates which is nothing but an ion-dipole interactions. From the tables 3 to 6 it is observed that adiabatic compressibility and free length goes on decreasing as concentration increases. Hence, there exists strong solute-solvent interaction i.e. ion-dipole interactions. It is also observed that free volume and acoustic impedance increases with increment in concentration and temperature which indicate strong association between solute and solvent.

CONCLUSIONS

It is general observed that ultrasonic velocity increased, as concentration increased. But in case of NaI the situation is reversed, it may be due to I^- ions. In both electrolytes sodium ion is common but anions are different. Iodide ion having greater size than chloride hence iodide ions break the structure of aqueous medium and affect stiffness of medium. Medium stiffness decides the ultrasonic velocity of medium.

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